FET Flagship Graphene

WP Energy (ramp-up phase)

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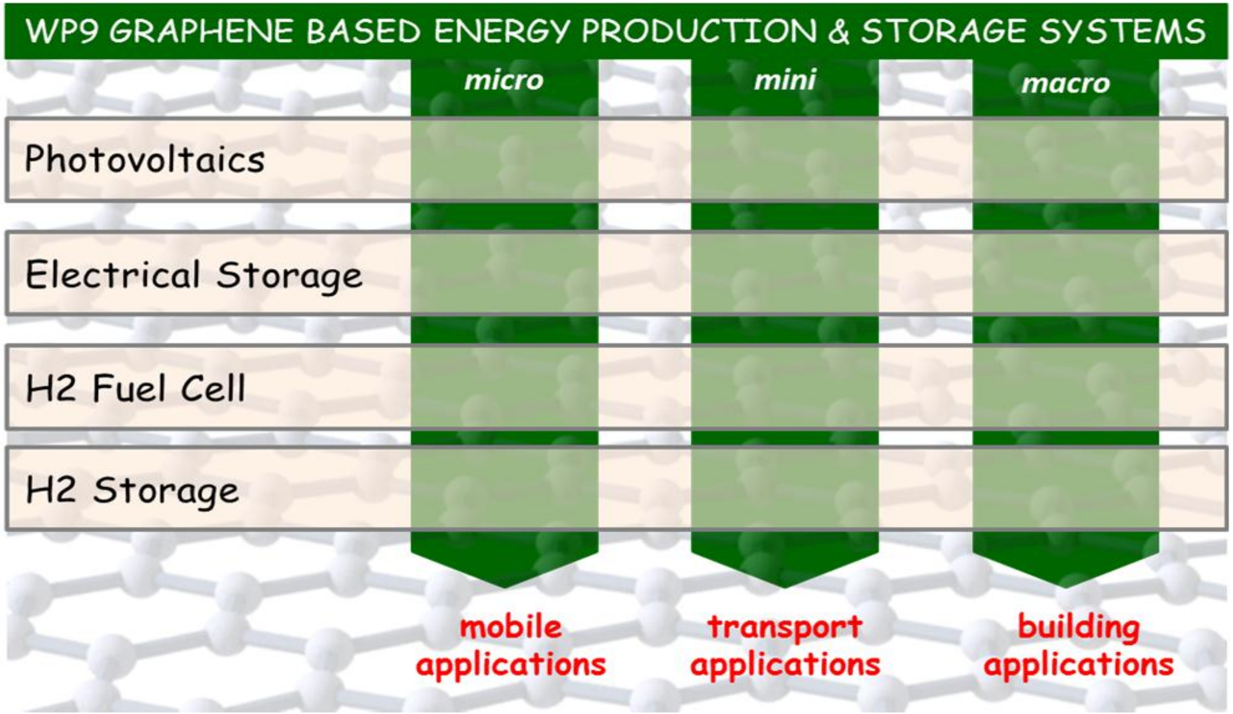
Scientific work packages

- WP1 Materials
- WP2 Health & Environment
- WP3 Fundamental science of graphene and 2D materials beyond graphene
- WP4 High Frequency Electronics
- WP5 Optoelectronics
- WP6 Spintronics
- WP7 Sensors
- WP8 Flexible Electronics
- WP9 Energy Applications
- WP10 Nanocomposites
- WP11 Production

WP9: 4 topics



WP9 GRAPHENE BASED ENERGY PRODUCTION & STORAGE SYSTEMS

	micro	mini	macro
Photovoltaics			
Electrical Storage			
H2 Fuel Cell			
H2 Storage			
	mobile applications	transport applications	building applications

In the 10-year perspective, this WP will develop and demonstrate the industrial potentials of key enabling graphene-based technologies for:

- Energy production systems: photovoltaics, fuel cells
- Energy storage systems: batteries, supercapacitors and hydrogen storage

Photovoltaics

Partners: CEA-Liten (CEA), Uni. Oxford (UOXF) , Italian Institute of technology (IIT), Technological Education Institute of Crete (TEIC).

Criteria: conversion efficiency, €/Wp

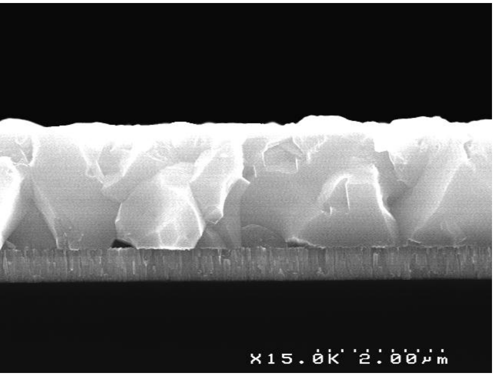
- 3 technological routes privileged:
    - Inorganic thin film PV: chalcogenide , wet process (CEA).
    - Organic PV (TEIC)
    - QD cells (IIT)

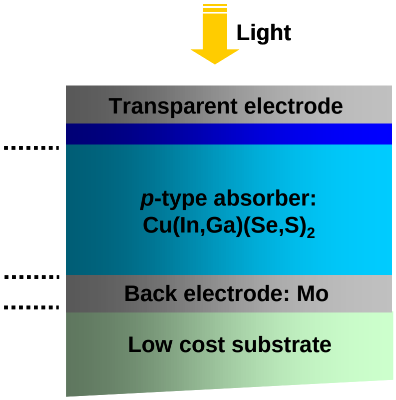
- Integration of Graphene:
    - Electrodes (e- and hole extraction layers),
    - Absorber layer.

- Support optronic modelling (UOXF)

Photovoltaics

- Chalcogenide (CIGS, CZTS) wet processed solar cells




Light

Transparent electrode

***p*-type absorber: $Cu(In,Ga)(Se,S)_2$**

Back electrode: Mo

Low cost substrate

10-year perspective

Conventional process	**Innovative wet process**
TCO by sputtering CdS : chemical bath	G-based electrode Cd-free buffer layer
co-evaporation or sputtering	CIGS or CZTS * by wet process
Sputtering	Sputtering

World record cell: PCE=**20.3%** in co-evaporation

Graphene top electrode

- Processed at 200°C max.
- R <30 Ω/□ and T >85%.

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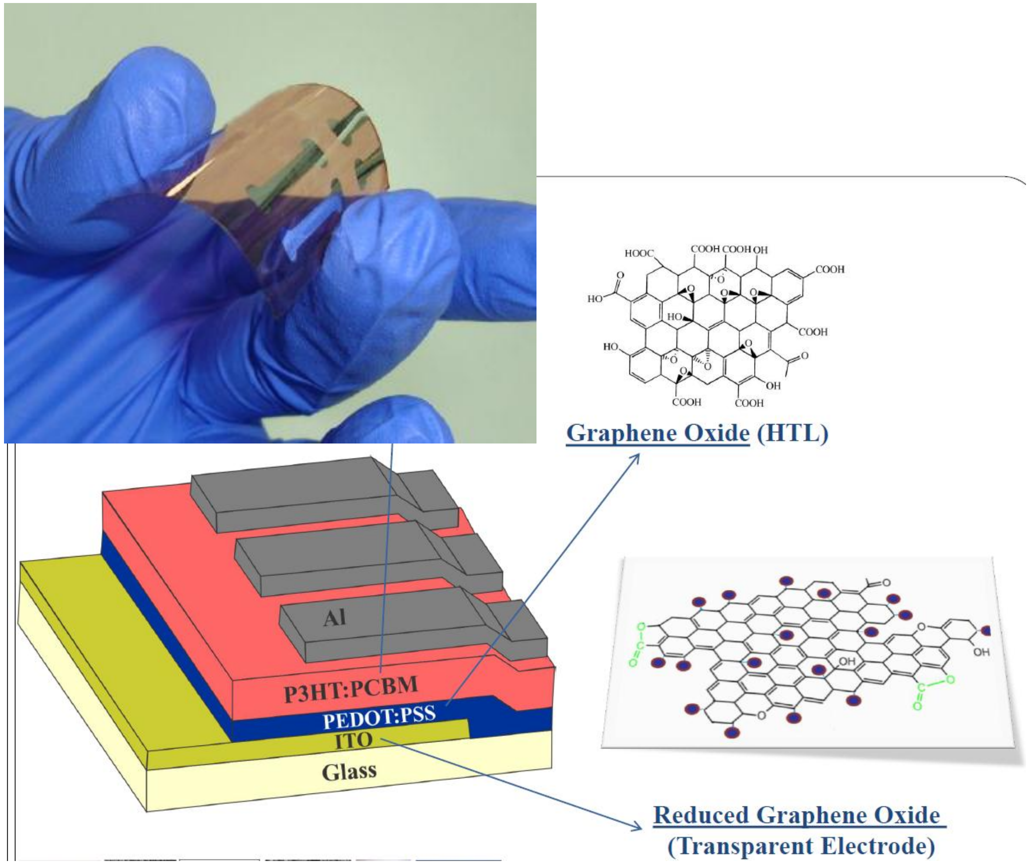
* $Cu_2ZnSn(S_{1-x}Se_x)_4$ based solar cell produced by selenization of vacuum deposited precursors
L. Grenet, S. Perraud et al, Solar Energy Materials & Solar Cells 101 (2012) 11.

Photovoltaics

- Organic solar cells: world record cell: η~**9%** in single junction (visible)



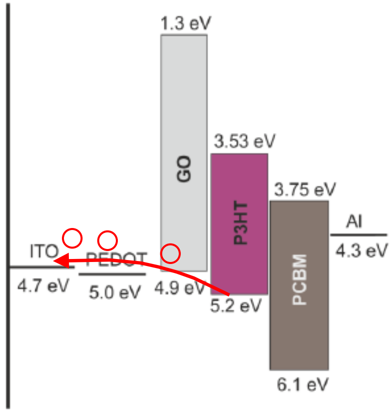
<u>Novel GO reduction approach: TCO electrodes</u>

Flexible OPV Cells with In Situ Non thermal Photoreduction
of Spin-Coated Graphene Oxide Electrodes
E. Kymakis et al., Adv. Funct. Mater. 2013, 1.

Present issues

<u>ITO</u>: scarcity, lack of flexibility, poor transparency in Near Infrared.

<u>PEDOT:PSS</u> : acidic solution, unstable.



Functionalized GO-based Hole Extraction Layer

- Replacement of PEDOT:PSS
- PCE>2.5%

Photovoltaics

❖ QD solar cells: tunable bandgaps for less thermalization losses

World record: PCE= **4.4%** with ZnO / PbS QD heterojunctions.

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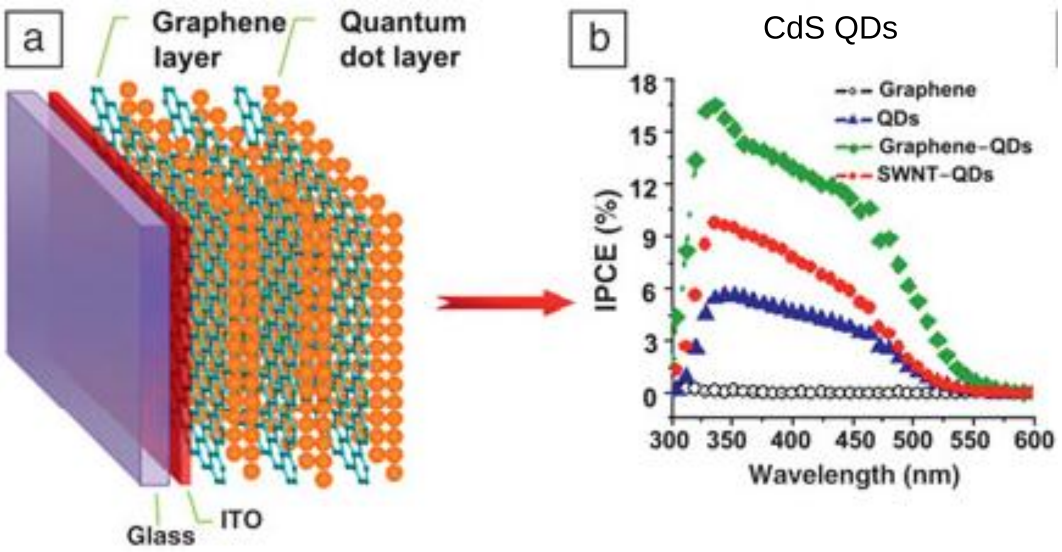

Present issues

Extraction of photo-carriers difficult!

High rate of recombinaisons

Operating solar cells with QD-functionalized graphene as PV absorber:

QD= $Cu_{2-x}S$ or $Cu_{2-x}Se$

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* C.X. Guo et al., Angew. Chem., Inte. Ed 49, 3014 (2010).

Proton Exchange Membrane Fuel Cells

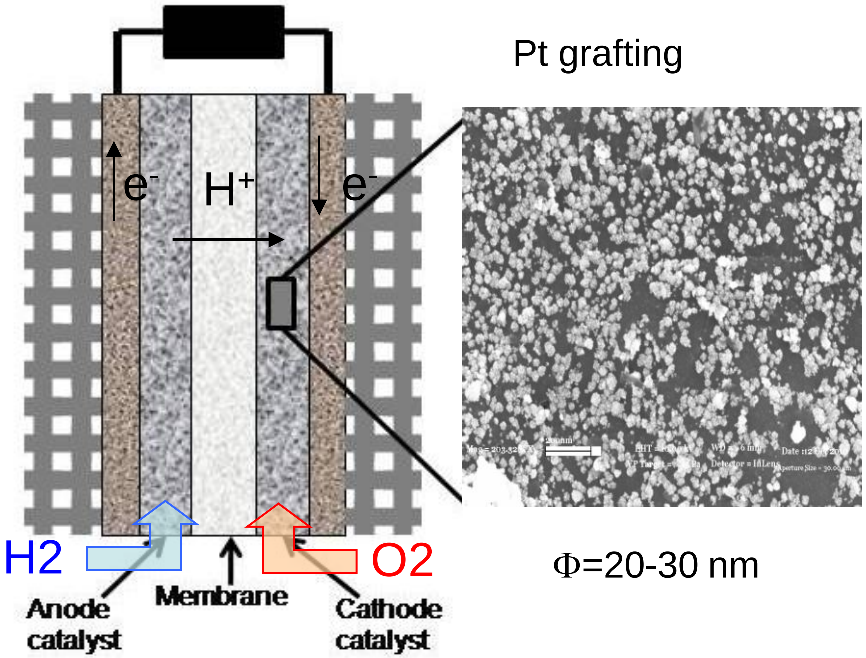
Partners: Sabancy University (SU)

Criteria: catalyst utilization efficiency W/g.Pt, lifetime.

- 2 technological routes privileged:
  - Pre-functionalization of G-sheets: control the Pt/Pt alloy catalyst grafting
  - Graphene-based nanocomposites (WP10)
- Integration of Graphene
  - Single fuel cells for electrical characterization.

Proton Exchange Membrane Fuel Cells

❖Use of functionalized G-sheets: better control of electrode surface area, conductivity, catalyst localization and water draining.



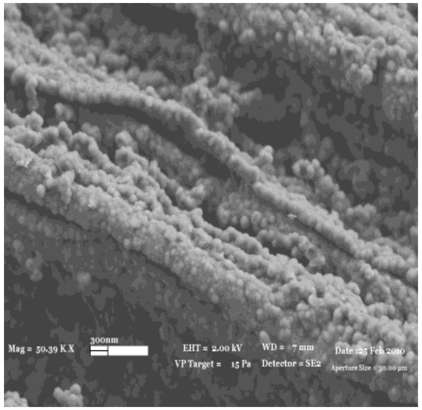
Pt grafting

Φ=20-30 nm

$H_2 \rightarrow 2H^+ + 2e^-$

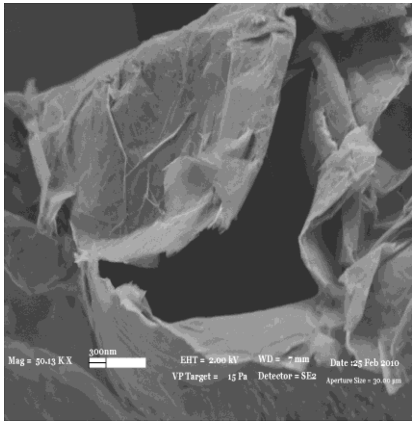
$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Polypyrrole coating, 13S/m



Promote anchoring and nucleation of catalyst

466 m²/g, 400S/m



G-sheets

Present issues

High Pt content (ink): ~0.4mg/cm2

Only a few % Pt is effective

5kW/g.Pt (SoA~1kW/gPt)

Saner, B. et al, Layer-by-Layer Polypyrrole Coated GO and G Nanosheets as Catalyst Support Materials for Fuel Cells, Fullerenes, Nanotubes, and Carbon nanostructures, 21: 233–247 (2013)

Batteries

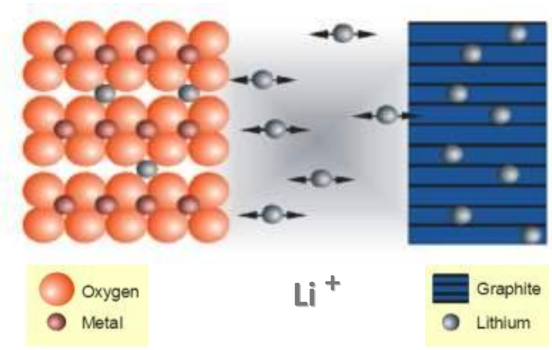
Partners: CEA-Liten (CEA), NOKIA.UKL, REPSOL (REP), Uni. Cambridge (UCAM), CIC Energygune (CIC).

Criteria: power density (kW/kg), energy density (Wh/kg), charging time, lifetime

- 3 technological routes:
  - GO-based route for the coating of electrodes (CEA).
  - Graphene/nanocrystals electrodes (UCAM).
  - Flexible electrodes: CVD graphene-Cu foil and graphene ink processing (NOKIA).
- Support characterisation activities
  - NMR characterisation during battery operation (UCAM).
  - Conventional battery testing (REP, CIC, CEA).
  - Dynamic modelling for lifetime prediction (REP).

Li^+ Batteries

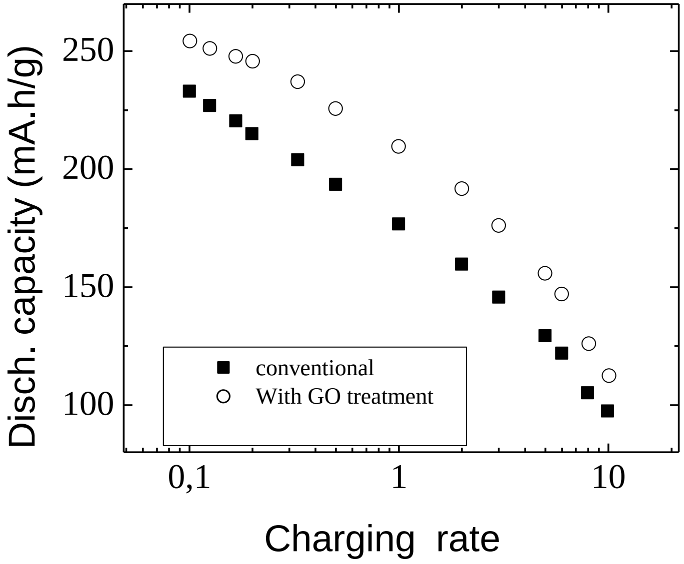
❖ GO-based route for the coating of electrodes: charging time

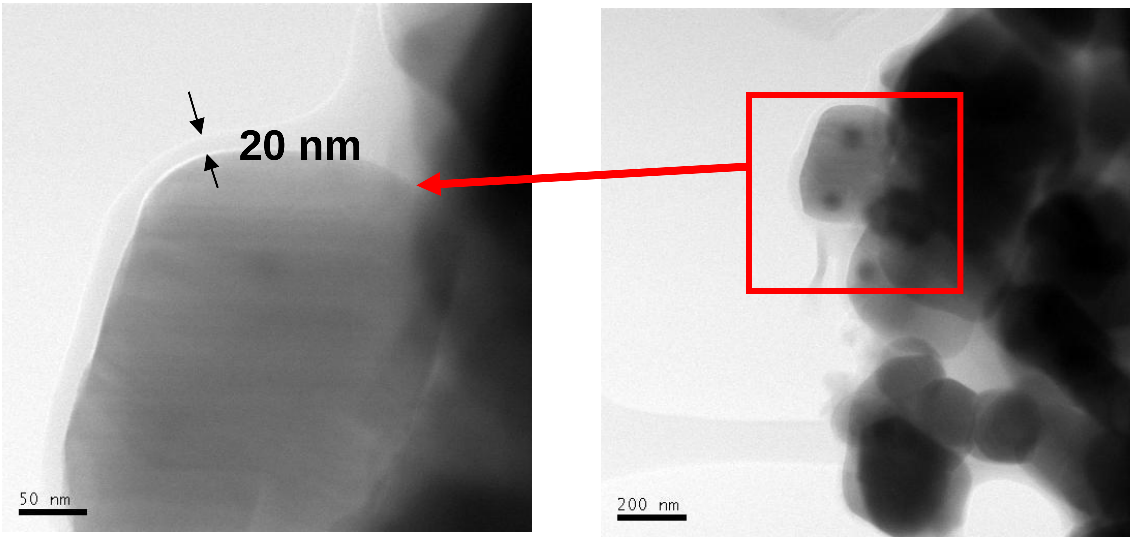


<u>Statement</u>:

- Most electrode active materials suffer from a poor conductivity ($LiFePO_4$, $LiMnPO_4$, Si, $L_{1+x}M_{1-x}O_2$, where M=Mn, Ni, Co, ...)

➢ Carbon coating by high T°C pyrolysis of C-precursors under controlled atmosphere: energy demanding.





Optimize GO process implementation

Better control of G thickness and structure

Li^+ Batteries

❖ Graphene/nanocrystals electrodes : lifetime.

Statement:

- Active materials suffer from huge volume changes during charging/discharging.
- Affect the cycle lifetime.

Use of nanocrystal-based hosting materials : Si for inst.

=> Requires nano-engineering

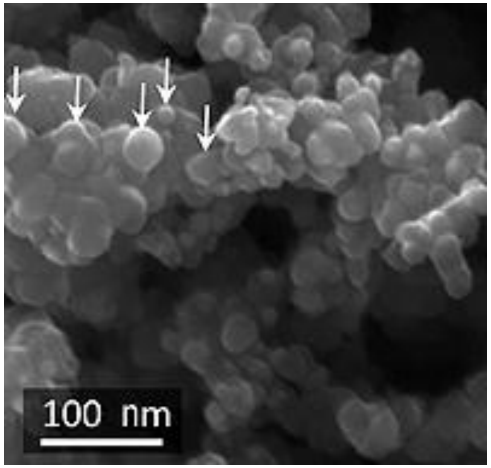
Flagship approach

- *Ex- situ* or *In-situ* growth of Si nCs between **graphene** layers.

- Porous FeOx ribbons grown on **graphene** (WP10)

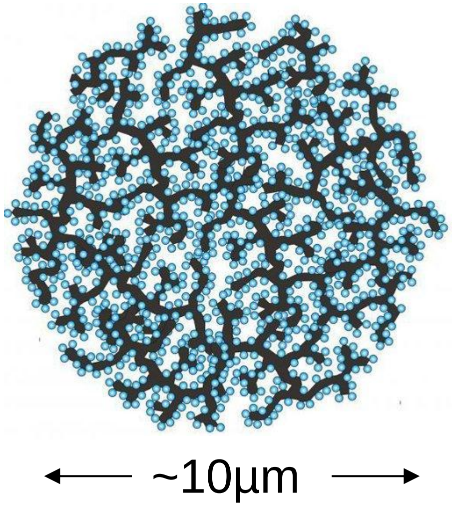
Battery with much higher cycle lifetime: >1000

C-coated Si nCs



Work done at Georgia Tech. (2010)

Granule made of Carbon interconnected Si nCs



Supercapacitors

Partners: CIC Energygune (CIC), Thales (TRT), Uni. Cambridge (UCAM).

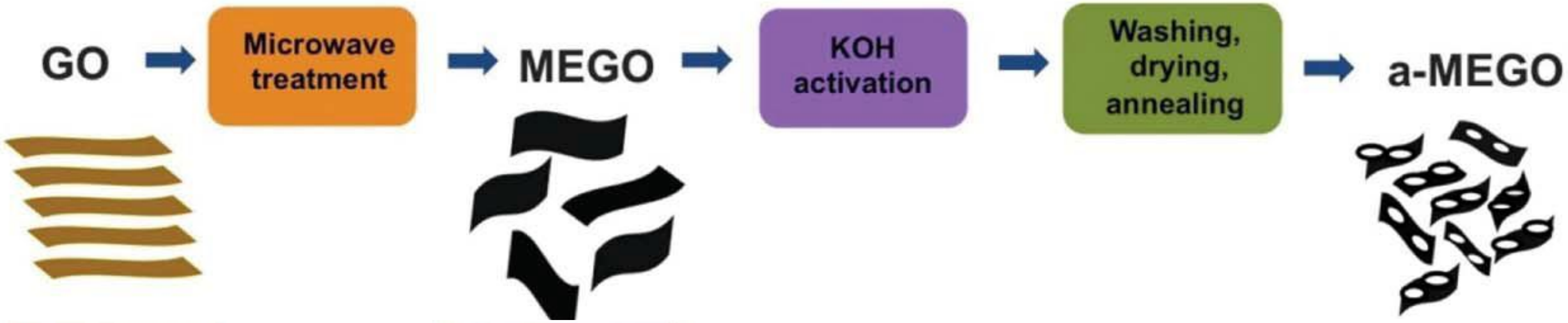
Criteria: power density (kW/kg) and energy density (Wh/kg)

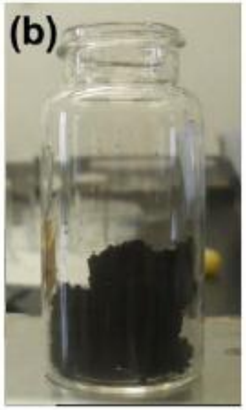
- 2 technological routes for electrochemical double layer capacitors:
  - GO-based route for the development of cost effective synthesis of electrodes (CIC).
  - Mesoporous electrodes combining CNT and graphene (TRT).
- Support characterisation activities
  - NMR characterisation: charging mechanisms versus electrode microstructure (UCAM)

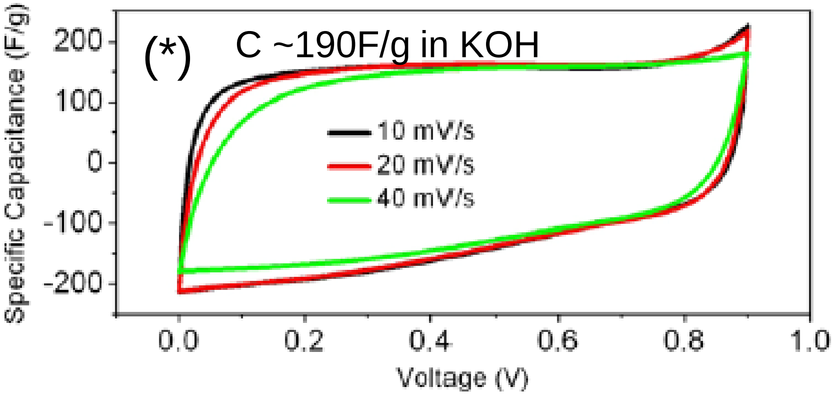
Supercapacitors

- GO-based route: Microwave process for cost effective synthesis of electrodes.

Objective: maximize the surface area of carbon electrodes


GO → Microwave treatment → MEGO → KOH activation → Washing, drying, annealing → a-MEGO




(*) C ~190F/g in KOH

Conductivity = 270 S/m
Surface area ~500 m^2/g

Target : >20Wh/Kg

* Ya. Zhu et al., Science 332, 1537 (2011)

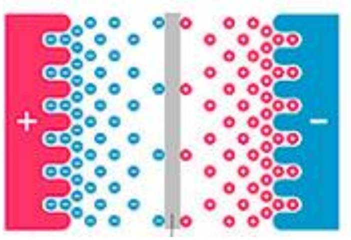
Supercapacitors

❖ Mesoporous electrodes combining CNT and graphene

Conventional process:

✓Electrode= activated carbon (high surface area).

✓Very small pores (1 nm) not easily accessible to ions of electrolyte.

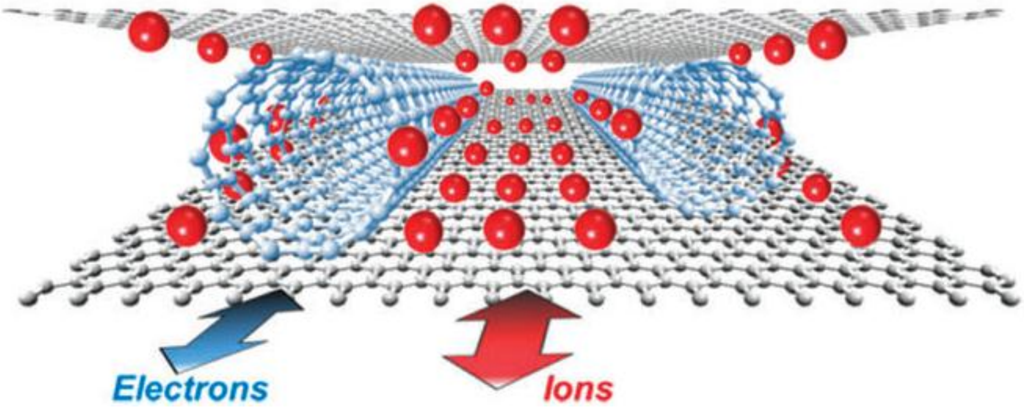


Innovative approach:

✓Use of a composite electrode: graphene + CNT.

✓ Recently demonstrated*:

- C= 290F/g in aqueous electrolyte.
- Energy density= 62Wh/Kg
- Power density= 58.5kW/Kg.



* *Q. Cheng, et al., Phys. Chem. Chem. Phys.,* ***2011,*** *13, 17615–17624,*

Hydrogen storage

Partners: CNR Pisa, Uni. Umea, Technical Uni. Dresden (TUDr), Bruno Kessler Foundation (FBK)

Criteria: storage capacity (Kg/m^3) and density (Wt%), ease of uptake/release of H_2

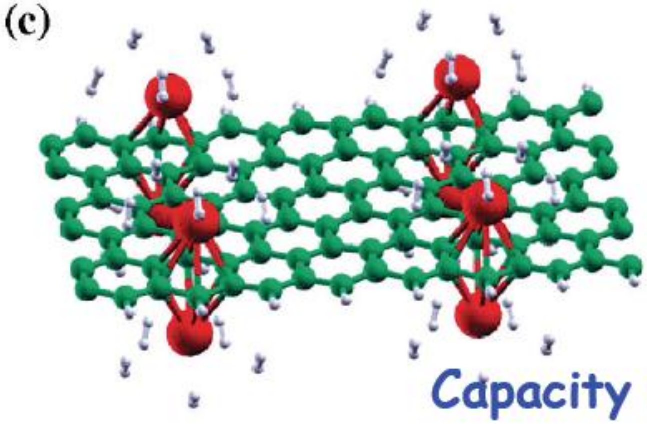
- 3 technological routes for the hosting material:
  - Decorated graphene with metal ad-atoms or molecular groups (FBK, UMEA, TUDr).
  - Intercalated multilayered graphene (UMEA)
  - Curved graphene sheets (CNR, UMEA).

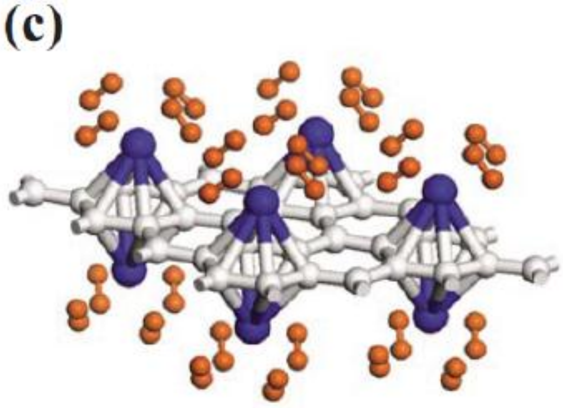
- Support activities
  - Modelling studies: interaction G-H2 with/without interlayer metal spacers, H2 storage capacity vs G-functionalization, etc… (CNR, TUDr)
  - Preliminary integration studies: testing tank (FBK).

Hydrogen storage

- ❖ Decorated graphene with metal ad-atoms or molecular groups
- ➢ tuning of surface kinetics of ad- and de-sorption reactions (H2-H spill-over process)

Modify graphene with various chemical species, such as Calcium or transisiton metals (Titanium) or Nitrogen





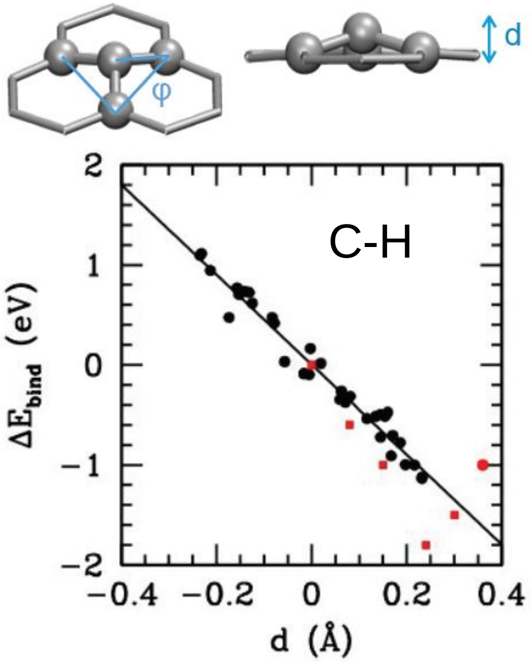
Capacity up to 5-9 wt%

Target: 3% wt% at RT

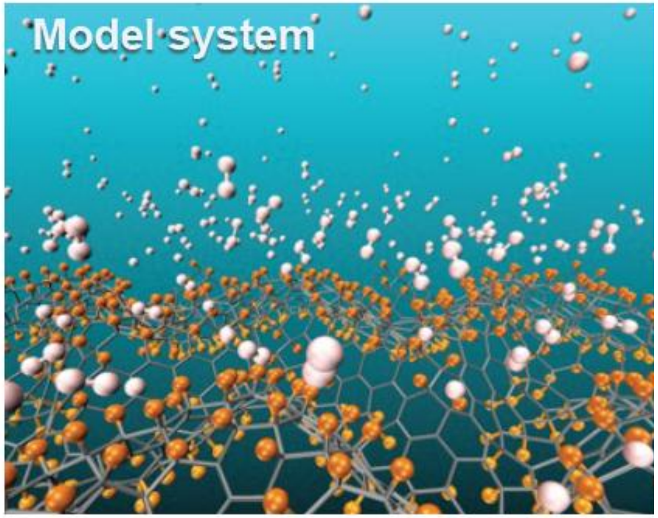
Hydrogen storage

❖ Curved graphene sheets

➢Control H2 uptake/release via graphene curvature



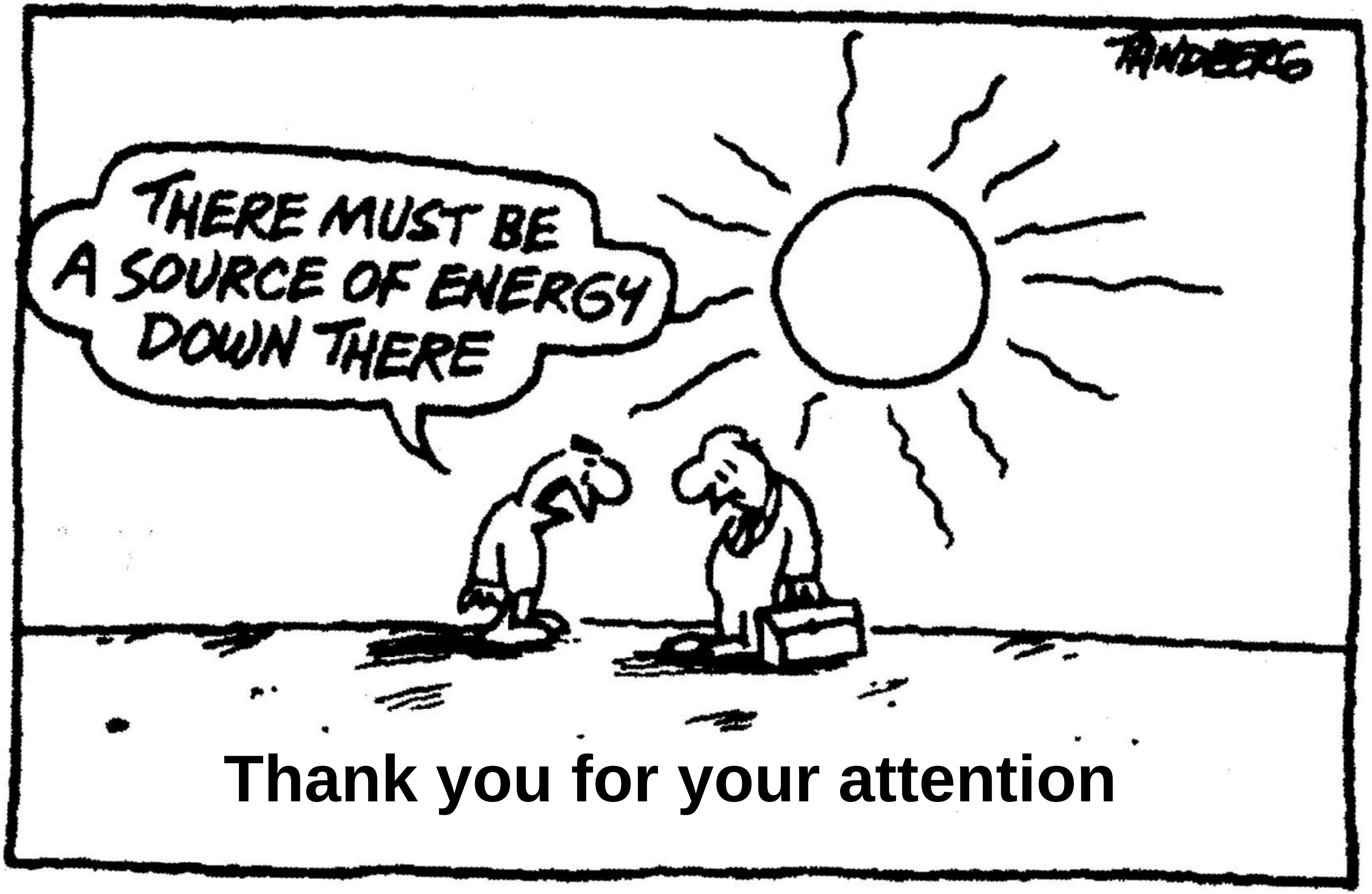
* Change with curvature of H binding E on graphene (modelling)



Experimental proof of concept of curvature effect.

Method to monitor the curvature?

* *V. Tozzini and V. Pellegrini, J. Phys. Chem. C, 115, 25523 (2011).*



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